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NEW COLUMN DESIGNS FOR MICROGC (PREPRINT)

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14. ABSTRACT
New column designs that give lower dispersion than column designs presented previously are presented. All of the work so far has concentrated on columns that are arranged with a spiral geometry. Spiral columns show lower dispersion than serpentines in chip scale electrophoresis and the assumption has been that spirals would also give lower dispersion than serpentines for microGC. We also test various turn geometries to see which gives the lowest dispersion. We have examined spiral and serpentine columns. We have also considered several turn geometries.

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NEW COLUMN DESIGNS FOR MICROGC

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ABSTRACT

In this paper, we present some new column designs for micro-gas chromatography (μGC) columns. Serpentine columns are compared to commonly used spiral columns and are found to give relatively lower height equivalent to theoretical plate (HETP) values. Turns are a major dispersion source for serpentine configuration. We found that sinusoidal compensation structures following the turns give lowest dispersion amongst the several tested turn geometries for serpentine configuration.

Keywords: microGC, microcolumns, dispersion in microchannels

I. INTRODUCTION

Many efforts are being made to develop a microfabricated gas chromatography (μGC) that is small enough to be carried by individuals [2-4]. Microcolumns are the heart of the GC technique. In this paper, we present some new column designs that give lower dispersion than the MEMS column designs presented previously [1-6].

Several recent papers have considered MEMS columns for μGC's [1-6]. All of the previous work has concentrated on columns that are arranged with a spiral geometry as shown in Figure 1a. Spiral columns show lower dispersion than serpentines in chip scale electrophoresis[7, 8] and the assumption has been that spirals would also give lower dispersion than serpentines for μGC columns. Note however, that the Dean number ($Dn = G\,w^3/\mu\,v\,(2w/R)^{1/2}$, which governs secondary flows in curved channels, where G is the centerline pressure gradient driving the primary flow, R is the channel radius of curvature, w is the channel width and μ and v are the fluid dynamic and kinematic viscosity respectively) is much larger in a gas than in a liquid. Consequently, the previous analysis for electrophoresis would not apply to a gas. Theoretically, when the Dean number is greater than 4, the dispersion in a spiral increases as the radius of curvature of the spiral decreases [7, 9-11]. In contrast, there is compensation in a serpentine column [7, 11, 12] so the dispersion does not increase as much as the size shrinks. The Dean number for the inner turns in the column in Figure 1A is over 200. The previous analysis done for electrohoresis does not apply. Thus, theoretically one does not know whether spirals or serpentines will work better as the size of the device shrinks. One also does not know how turn geometry affects performance.

In this paper we consider a number of different geometries. We compare a serpentine to a spiral. We also test various turn geometries to see which gives the lowest dispersion.

II. DESIGN AND FABRICATION

Figure 1 shows the two configurations: spiral and serpentine fabricated on silicon. The microchannels are 3 meters long and 100 microns wide etched 100 microns deep using DRIE. The columns were connected to a 200 micron OD
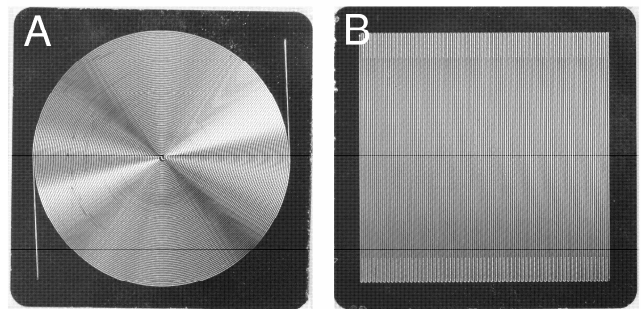

Figure 1. Pictures of A) spiral and B) serpentine columns
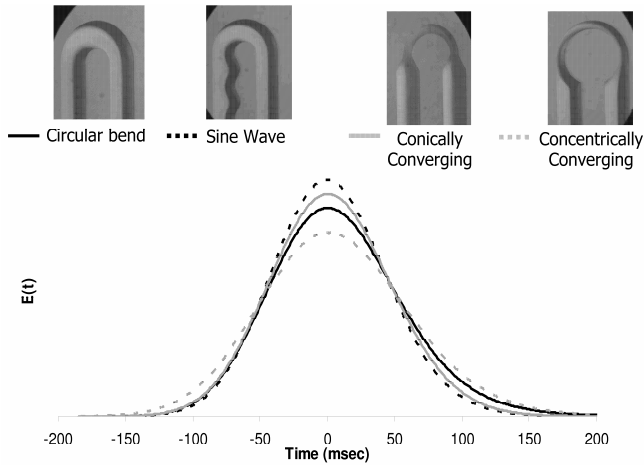
Figure 2. The methane peaks observed on serpentine columns with different turn geometries measured on a 0.3 m long column. Notice that the sine wave bends give lower dispersion than any of the other geometries

fused silica capillary using a package designed in-house.

The serpentine configuration would cause maximum dispersion at the turns. Three new turn geometries are tested with respect to the dispersion generated by a simple circular bend: (1) circular turn with a sine wave compensation structure, (2) a conically converging turn, and (3) a concentrically converging turn. See Figure 2,. The sine wave compensation structure was designed to reduce the strength of the Dean vortex using a series of expansions and contractions. The conically converging turns are adopted from the microcapillary electrophoresis literature to minimize dispersion due to race-track effect. The distortion in a band traveling about a turn is reduced if the width of the channel is reduced. Concentrically converging turn is an adaptation of the prior turn wherein the inner path bulges out to a certain radius to produce contraction at the turn. Comparison of the new turn designs to the circular turn was performed using 30 cm long microchannel chip with 22 pairs of turns fabricated on silicon.

We used the following fabrication sequence to generate 3 meter long microcolumns for testing the different μGC columns. The fabrication process starts with a (100) silicon wafer with 2

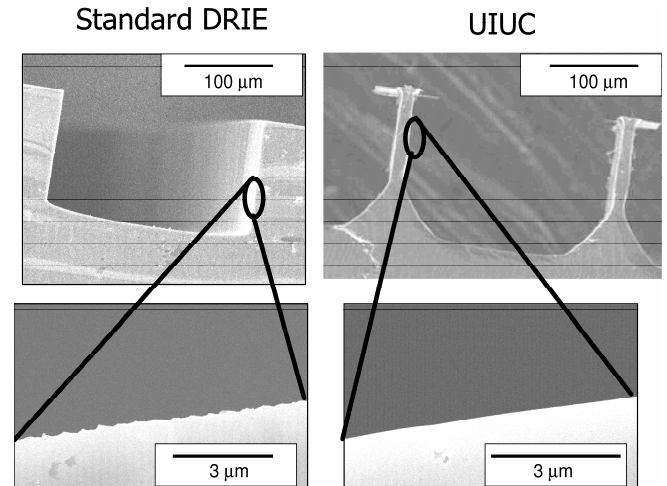μm thick thermally grown oxide. (a) Photoresist (PR)

Figure 3. The effect of the UIUC process to smooth the sidewalls and round the corners of a microGC column.

S1813 is patterned for the channels and connection holes. (b) Oxide is patterned using CF_4 RIE. (c) PR is stripped and DRIE is performed on column side first to yield 100 micron deep channels. DRIE is performed on the second side to etch the access holes through the silicon wafer, simultaneously dicing the wafer. (f) We found that channel walls can be smoothened using two processes: (1) growing 2 μm thick wet oxide followed by BOE etching, and (2) growing porous silicon using anodization followed by its removal with mild KOH. Figure 3 shows the resultant shaping and smoothening of the column walls obtained with anodization process. (e) The μGC column dies are cleaned with BOE, SC-1 and SC-2 sequentially. (f) SC-1 cleaned Pyrex 7740 coverslips are anodically bonded to yield sealed microcolumns.

III. COLUMN PERFORMANCE TESTING

The silicon microcolumn is packaged to connect 15 cm long, 0.1 micron ID deactivated fused silica tubing, which is used to connect the microcolumn to an Agilent 6890N GC injection system and flame ionization detector system. One microliter of methane and iso-octane headspaces are injected with a split ratio of 100:1. The

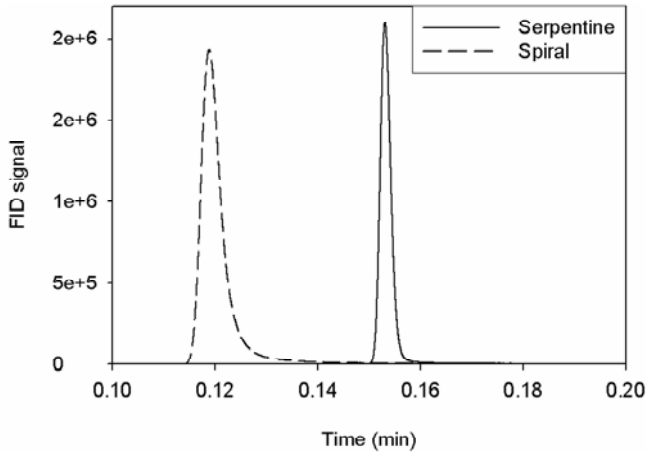column efficiency is measured with methane and iso-octane at 110°C.

Figure 4. A comparison of the methane peaks seen with a 3 meter long 100 micron wide and deep serpentine and spiral channels that had undergone smoothing and rounding (see text). The measurements were done with a 20 psi hydrogen sweep gas.

IV. RESULTS AND DISCUSSION

Figure 4 shows the elution profiles of a methane pulse from a serpentine column and a spiral column. The methane pulse eluting from a serpentine column tails less and shows half the pulse width relative to spiral column. Figure 5 shows the plot of calculated height equivalent to theoretical plates (HETP) versus average carrier gas velocity (u) to generate Golay plots of the methane injections. The Golay plots are theoretically modeled, shown as lines in Fig. 5, using the Golay-Guocheon kinetic model for
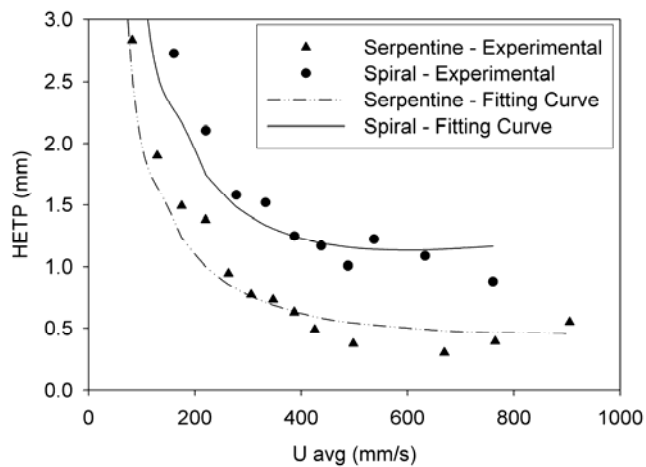

Figure 5. Golay plots for methane injections in 100 micron diameter, 3 meter long serpentine and spiral columns.
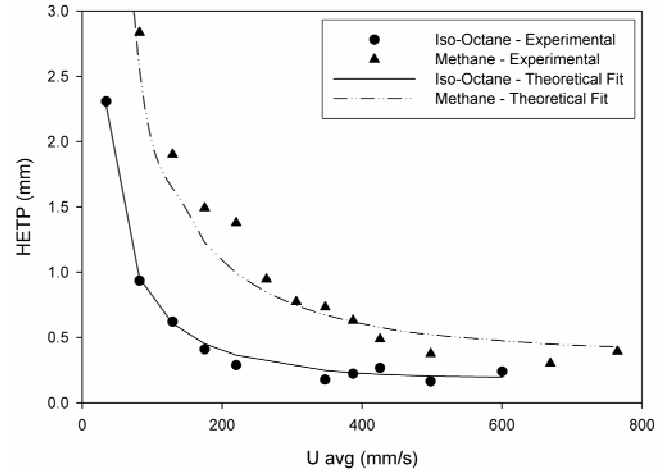

Figure 6. Golay plots for methane and iso-octane separation in 100 micron diameter, 3 meter long serpentine column.

column efficiency,

$$HETP = \frac{B}{u} + Cu + Du^2$$

where B is the coefficient for longitudinal diffusion, C is for resistance to mass transport in the gas phase and D is for extracolumn band broadening. Serpentine columns give lower HETP values compared to the spiral columns.

Figure 6 shows the difference between the Golay plots obtained using methane and iso-octane as tracer molecule in efficiency calculations at same operating conditions. We find that the HETP value decreases as the molecular weight increases, as expected from Taylor-Aris dispersion theory.
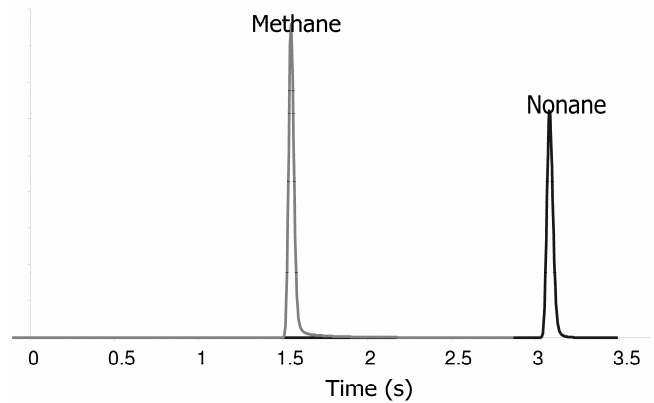

Figure 7. The methane and nonane peaks seen in the 3 meter column at high velocity

Figure 2 compares methane pulses eluted from 30 cm long serpentine columns with different turn geometries. The sinusoidal compensation structured turn gives the lowest dispersion amongst all compared. Figure 7 shows peaks we have measured on the columns. These columns show peak capacities of about 90 in 4 seconds using hydrogen as a carrier gas. This compares to a peak capacity of 5 in 4 seconds reported by Reidy *et al.* [1] using air as a sweep gas. These results show that wall smoothing and device design have an important influence on column performance.

V. CONCLUSIONS

We have investigated design rules for μGC columns. We have successfully tested and compared performance of spiral and serpentine columns and various bend geometries for μGC separation. Serpentine columns give the lowest dispersion since the small spiral columns generate an overall higher Dean vortices when integrated over all the column. Sinusoidal compensation structures help reduce the dispersion caused by a normal circular turn. These findings will enable future μGC researchers to design higher efficiency columns.

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